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- (71) Applicant (*for all designated States except US*): **BOREALIS TECHNOLOGY OY** [FI/FI]; P.O. Box 330, FIN-06101 Porvoo (FI).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **ANDELL, Ove** [SE/FI]; Merikortitie 13 as. 407, FIN-00960 Helsinki (FI). **MAARANEN, Janne** [FI/FI]; Heisitie 1 B, FIN-04260 Kerava (FI). **KETOLA, Lasse** [FI/FI]; Lahdepolku 3-4, D 36, FIN-06100 Porvoo (FI).
- (74) Agents: **CAMPBELL, Neil et al.**; Frank B. Dehn & Co., 179 Queen Victoria Street, London EC4V 4EL (GB).
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**WO 01/70395 A2**

(54) Title: CATALYSTS

(57) Abstract: A metallocene procatalyst compound comprising a group III element or a group 3 to 8 transition metal  $\eta$ -bonded by an open  $\eta^5$ -ligand having at least two heteroatoms in the five atom  $\eta^5$  chain and having an unsaturated ring fused to the first and second atoms of the  $\eta^5$  chain and a further unsaturated ring fused to the fourth and fifth atoms of the  $\eta^5$  chain.

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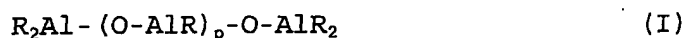
## CATALYSTS

5 This invention relates to catalysts for olefin polymerisation, in particular to catalyst compounds containing metals  $\eta$ -bonded by open- $\eta^5$ -ligands, and their use in olefin polymerisation.

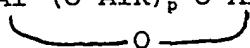
10 In olefin polymerization, it has long been known to use as a catalyst system the combination of a metallocene procatalyst and an alumoxane co-catalyst.

By "metallocene" is here meant an  $\eta$ -ligand metal complex, e.g. an "open sandwich" or "half sandwich" compound in which the metal is complexed by a single  $\eta$ -ligand, a "sandwich" compound in which the metal is complexed by two or more  $\eta$ -ligands, a "handcuff" compound in which the metal is complexed by a bridged bis- $\eta$ -ligand or a "scorpionate" compound in which the metal is complexed by an  $\eta$ -ligand linked by a bridge to a  $\sigma$ -ligand.

20 Alumoxanes are compounds with alternating aluminium and oxygen atoms generally compounds of formula I or II



25



30 where each R, which may be the same or different, is a  $C_{1-10}$  alkyl group, and p is an integer having a value between 0 and 40). These compounds may be prepared by reaction of an aluminium alkyl with water. The production and use of alumoxanes is described in the patent literature, especially the patent applications of Texas Alkyls, Albemarle, Ethyl, Phillips, Akzo Nobel, Exxon, Idemitsu Kosan, Witco, BASF and Mitsui.

35 We have now found a novel class of  $\eta$ -ligand complexes that can function as olefin polymerization catalysts. In these complexes a group III element or a

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group 3 to 8 transition metal is  $\eta$ -bonded by a five atom chain which, unlike in standard metallocenes, is not a closed ring structure, i.e. the five atoms do not form a closed ring. Such a ligand is referred to herein as an  
5 "open  $\eta^5$  ligand".

Viewed from one aspect therefore the invention provides a metallocene procatalyst compound comprising a group III element or a group 3 to 8 transition metal  $\eta$ -bonded by an open  $\eta^5$ -ligand having at least two  
10 heteroatoms (e.g. Si, P, B and N) in the five atom  $\eta^5$  chain and having an unsaturated ring (e.g. a 4 to 12 atom ring) fused to the first and second atoms of the  $\eta^5$  chain and a further unsaturated ring fused to the fourth and fifth atoms of the  $\eta^5$  chain.

15 In the  $\eta^5$  chain, the third atom is preferably C or Si, especially C and is optionally substituted, preferably by a group which also bonds to the transition metal, e.g. which  $\sigma$ -bonds or  $\eta$ -bonds the metal. In a most preferred embodiment the atoms at positions 1 and 5  
20 of the  $\eta^5$  chain are nitrogen whilst the atoms at positions 2, 3 and 4 are carbon.

The rings fused to the  $\eta^5$ -chain may conveniently contain up to 4 ring heteroatoms, preferably selected from N, P and B. Such rings moreover may be substituted  
25 and may carry further fused rings. Particularly preferably such rings are part of monocyclic or fused bicyclic groups. The rings fused to the  $\eta^5$  chain are especially preferably aromatic. Where the rings fused to the  $\eta^5$  chains are non-aromatic, the ring atoms of the  
30 fused rings adjacent the 1 or 5 atoms of the  $\eta^5$  chain are preferably substituted by optionally halogenated (e.g. fluorinated) alkyl, aryl, aralkyl or arylalkyl groups, e.g. containing up to 12 carbons.

By group 3 (etc) metal is meant a metal in group 3  
35 of the Periodic Table of the Elements, namely Sc, Y, La and Ac; by group 4 is meant Ti, Zr, Hf etc. By group III element is meant B, Al, Ga, In, Tl.

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Viewed from a further aspect the invention provides an olefin polymerisation catalyst system comprising or produced by reaction of (i) a metallocene procatalyst compound comprising a group III element or a group 4 to 8 transition metal  $\eta$ -liganded by an open  $\eta^5$ -ligand having at least two heteroatoms (e.g. Si, P, B and N) in the five atom  $\eta^5$  chain and having an unsaturated ring (e.g. a 4 to 12 atom ring) fused to the first and second atoms of the  $\eta^5$  chain and a further unsaturated ring fused to the fourth and fifth atoms of the  $\eta^5$  chain and (ii) a co-catalyst, eg an aluminium alkyl compound, in particular an alumoxane.

Viewed from a still further aspect the invention provides a process for olefin polymerisation comprising polymerising an olefin in the presence of a metallocene compound comprising a group III element or a group 3 to 8 transition metal  $\eta$ -liganded by an open  $\eta^5$ -ligand having at least two heteroatoms (e.g. Si, P, B and N) in the five atom  $\eta^5$  chain and having an unsaturated ring (e.g. a 4 to 12 atom ring) fused to the first and second atoms of the  $\eta^5$  chain and a further unsaturated ring fused to the fourth and fifth atoms of the  $\eta^5$  chain.

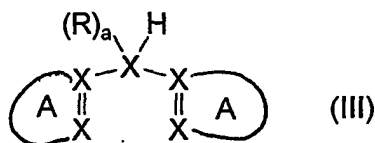
Viewed from a yet further aspect the invention provides a process for the preparation of a metallocene procatalyst, said process comprising metallating with a group III element or a group 3 to 8 transition metal an open  $\eta^5$ -ligand having at least two heteroatoms (e.g. Si, P, B and N) in the five atom  $\eta^5$  chain and having an unsaturated ring (e.g. a 4 to 12 atom ring) fused to the first and second atoms of the  $\eta^5$  chain and a further unsaturated ring fused to the fourth and fifth atoms of the  $\eta^5$  chain.

Viewed from a further aspect the invention provides the use of a metallocene compound comprising a group III element or a group 3 to 8 transition metal  $\eta$ -liganded by an open  $\eta^5$ -ligand having at least two heteroatoms (e.g. Si, P, B and N) in the five atom  $\eta^5$  chain and having an

unsaturated ring (e.g. a 4 to 12 atom ring) fused to the first and second atoms of the  $\eta^5$  chain and a further unsaturated ring fused to the fourth and fifth atoms of the  $\eta^5$  chain in olefin polymerization, especially ethylene or propylene, more especially ethylene, polymerisation or copolymerisation.

Viewed from a yet further aspect the invention provides an olefin polymer produced by a polymerisation catalysed by a metallocene compound comprising a group  
10 III element or a group 3 to 8 transition metal  $\eta$ -liganded by an open  $\eta^5$ -ligand having at least two heteroatoms (e.g. Si, P, B and N) in the five atom  $\eta^5$  chain and having an unsaturated ring (e.g. a 4 to 12  
atom ring) fused to the first and second atoms of the  $\eta^5$   
15 chain and a further unsaturated ring fused to the fourth and fifth atoms of the  $\eta^5$  chain.

The open  $\eta^5$ -ligand with which the group III element or group 3 to 8 metal is complexed typically is a compound of formula III



25 where  $\begin{matrix} \text{X} \\ \text{C} \\ \text{A} \text{---} \text{I} \\ \text{X} \end{matrix}$  is an optionally substituted 5 to 12  
membered ring;

each X independently is C, N, P, B or Si, at least  
30 two X's being heteroatoms, preferably N, P or B;  
a is 0 or 1;

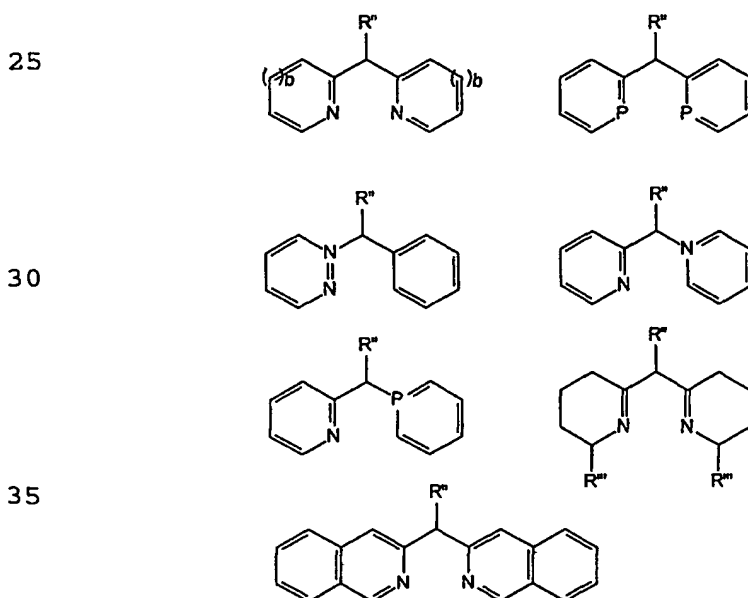
R is a C<sub>1-16</sub> hydrocarbyl, a tri C<sub>1-8</sub> hydrocarbylsilyl or a tri C<sub>1-8</sub> hydrocarbylsiloxy group or a group R<sup>a</sup>R<sup>b</sup> where R<sup>a</sup> is a 1 to 4 atom bridge (preferably containing C, N or Si bridge atoms) and R<sup>b</sup> is a group capable of σ-bonding or η-bonding a transition metal (e.g. η-bonding ligands such as a homo or heterocyclic cyclopentadienyl, indenyl, fluorenyl, octahydrofluorenyl,

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methylcyclopentadienyl, 1,2-dimethylcyclopentadienyl,  
 pentamethylcyclopentadienyl, pentyl-cyclopentadienyl,  
 2-dimethyl-tertbutylsiloxy-inden-1-yl,  
 n-butylcyclopentadienyl, 1,3-dimethylcyclopentadienyl,  
 5 4,7-dimethylindenyl, 1-ethyl-2-methylcyclopentadienyl,  
 tetrahydroindenyl, and methoxycyclopentadienyl or  
 $\sigma$ -ligands such as halogenides (e.g. chloride and  
 fluoride), hydrogen, tri- $C_{1-12}$  hydrocarbyl-silyl or  
 -siloxy (e.g. trimethylsilyl),  
 10 tri- $C_{1-6}$  hydrocarbylphosphimido (e.g.  
 triisopropylphosphimido),  $C_{1-12}$  hydrocarbyl or  
 hydrocarbyloxy (e.g. methyl, ethyl, phenyl, benzyl and  
 methoxy), di- $C_{1-6}$  hydrocarbylamido (e.g. dimethylamido and  
 diethylamido), and 5 to 7 ring membered heterocyclyl (eg  
 15 pyrrolyl, furanyl and pyrrolidinyl), or an amido group).

In the ligands of formula III, bridge or ring atoms  
 may if desired be substituted by groups  $R'$ , where each  
 $R'$  which may be the same or different is a  $R^+$ ,  $OR^+$ ,  $SR^+$ ,  
 $NR_2^+$  or  $PR_2^+$  group where each  $R^+$  is a  $C_{1-16}$  hydrocarbyl  
 20 group, a tri- $C_{1-8}$  hydrocarbylsilyl group or a tri- $C_{1-8}$ -  
 hydrocarbylsiloxy group, preferably  $R'$  being a  $C_{1-12}$   
 hydrocarbyl group, eg a  $C_{1-8}$  alkyl or alkenyl group;

Examples of ligands of formula III include:



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where b is 1, 3, 5 or 7;

R" is H or a  $\sigma$ - or  $\eta$ -liganding group; and

R"' is optionally fluorinated C<sub>1-6</sub> alkyl or phenyl, e.g. CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, CF<sub>3</sub> or C<sub>6</sub>F<sub>5</sub>.

5 Besides the  $\eta$ -ligand of formula III, the group III element or group 3 to 8 transition metal may be  $\eta$ -liganded by one or two further  $\eta$  ligands. These may be cyclic or acyclic and may carry cyclic groups fused to an  $\eta^5$  or  $\eta^4$  cyclic or acyclic structure and may be  
10 bridged bis- $\eta$  ("handcuff") ligands or bridged  $\eta$ - $\sigma$  ("scorpion") ligands. Thus for example such an  $\eta^5$  or  $\eta^4$  ligand group may be a homo- or heterocyclic cyclopentadienyl, indenyl or fluorenyl group, or an acyclic  $\eta^5$  C<sub>5</sub>,  $\eta^5$ -C<sub>3</sub>N<sub>2</sub> or  $\eta^4$ C<sub>2</sub>N<sub>2</sub> group optionally carrying  
15 cyclic groups fused to the  $\eta^5$  or  $\eta^4$  skeleton. Such further  $\eta$  ligands may optionally be substituted, eg by groups R'.

Particular examples of such further  $\eta$ -ligands include cyclopentadienyl, indenyl and fluorenyl ligands, especially siloxy substituted (eg R'<sub>3</sub>SiO-substituted)  
20 cyclopentadienyl or indenyl ligands.

Examples of such further  $\eta$ -ligands abound in the patent literature relating to metallocene and pseudo metallocene olefin polymerization (pro)catalysts, in particular that deriving from Exxon, Hoechst, Phillips,  
25 Dow, Chisso, Mitsui, Fina, BASF, Mitsubishi, Mobil, Targor, DSM and Borealis, eg WO96/23010, WO98/49208, WO99/12981, WO99/19335, WO97/28170, EP-A-423101, EP-A-537130, etc. as well as "Metallocenes" Vol. 1, Togni and  
30 Halterman (Eds.) Wiley-VCH, 1998.

Besides  $\eta$ -ligands, the group III element or group 3 to 8 metal in the procatalyst of the invention may be coordinated by hydrogen atoms, hydrocarbyl  $\sigma$ -ligands (eg optionally substituted C<sub>1-12</sub> hydrocarbyl groups, such as  
35 C<sub>1-12</sub> alkyl, alkenyl or alkynyl groups optionally substituted by fluorine and/or aryl (eg phenyl) groups), by silane groups (eg Si(CH<sub>3</sub>)<sub>3</sub>), by halogen atoms (eg

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chlorine), by C<sub>1-8</sub> hydrocarbylheteroatom groups, by tri-C<sub>1-8</sub>hydrocarbylsilyl groups, by bridged bis-σ-liganding groups, by amine (eg N(CH<sub>3</sub>)<sub>2</sub>) or imine (eg N=C or N=P groups, eg R<sub>3</sub>P=N- wherein each R can be

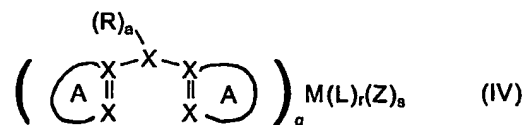
5 independently the same or different, aliphatic or aromatic hydrocarbyl with 1 to 12 C atoms, or by other σ-ligands known for use in metallocene (pro)catalysts.

By a σ-ligand moiety is meant a group bonded to the metal at one or more places via a single atom, eg a

10 hydrogen, halogen, silicon, carbon, oxygen, sulphur or nitrogen atom.

Thus for example the metallocene procatalyst of the invention may conveniently be a compound of formula (IV)

15



20

where  $\begin{array}{c} \text{X} \\ \text{A} \parallel \text{X} \end{array}$ , (R)<sub>a</sub>, and X are as hereinbefore defined;

q is 1, 2 or 3, generally being 1;

M is a group III element or group 3 to 8 transition

25 metal

L is a further η-ligand (eg as discussed above);

r is zero, 1 or 2;

Z is a σ-ligand (eg as discussed above); and

s is zero or a positive integer having a value of up to

30 3 depending on the values of q and r and the oxidation state of metal M.

The metal M in the metallocene procatalysts of the invention is preferably aluminium or a group 4 to 8 transition metal, preferably a group 4 to 6 transition

35 metal, eg a metal selected from Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W. However the metal is preferably Ti, Zr, Al or Hf.

In the metallocene procatalysts of the invention,

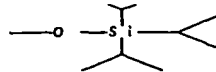
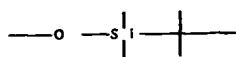


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the open  $\eta^5$ -ligand and any other  $\eta$ -ligands preferably carry a siloxy substituent  $R'_3SiO$ .

Examples of suitable  $R'_3SiO$  groups in the metallocene procatalysts of the invention include

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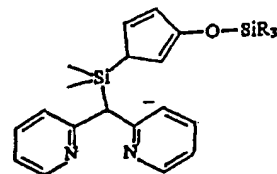
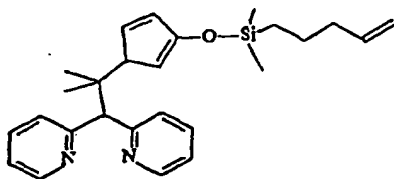
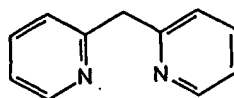
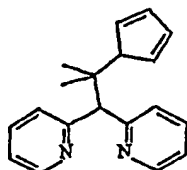
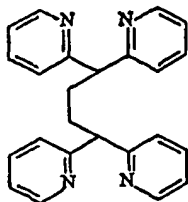
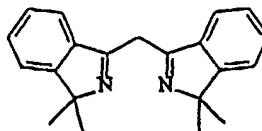
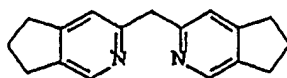
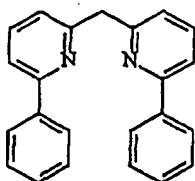
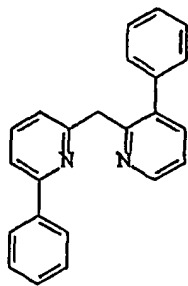
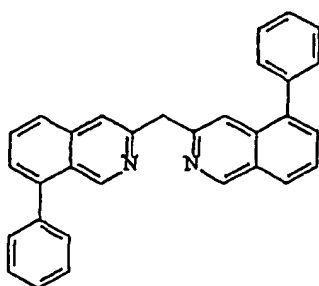


and



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Examples of particular open  $\eta^5$ -ligands usable according to the invention include:



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Examples of particular further  $\eta$ -ligands are well known from the technical and patent literature relating to metallocene olefin polymerization catalysts, e.g. EP-A-35242 (BASF), EP-A-129368 (Exxon), EP-A-206794

5 (Exxon), PCT/FI97/00049 (Borealis), EP-A-318048, EP-A-643084, EP-A-69951, EP-A-410734, EP-A-128045, EP-B-35242 (BASF), EP-B-129368 (Exxon) and EP-B-206794 (Exxon).

These include

10 cyclopentadienyl,  
indenyl,  
fluorenyl,  
octahydrofluorenyl,  
methylcyclopentadienyl,  
15 1,2-dimethylcyclopentadienyl,  
pentamethylcyclopentadienyl,  
pentyl-cyclopentadienyl,  
2-dimethyl,tertbutylsiloxy-inden-1-yl,  
n-butylcyclopentadienyl,  
20 1,3-dimethylcyclopentadienyl,  
4,7-dimethylindenyl,  
1,-ethyl-2-methylcyclopentadienyl,  
tetrahydroindenyl, and  
methoxycyclopentadienyl.

25

Examples of  $\sigma$ -ligands include:

halogenides (e.g. chloride and fluoride),  
hydrogen,  
30 triC<sub>1-12</sub> hydrocarbyl-silyl or -siloxy (e.g. trimethylsilyl),  
triC<sub>1-6</sub> hydrocarbylphosphimido (e.g. triisopropylphosphimido),  
C<sub>1-12</sub> hydrocarbyl or hydrocarbyloxy (e.g. methyl, ethyl,  
35 phenyl, benzyl and methoxy),  
diC<sub>1-6</sub> hydrocarbylamido (e.g. dimethylamido and diethylamido), and

- 10 -

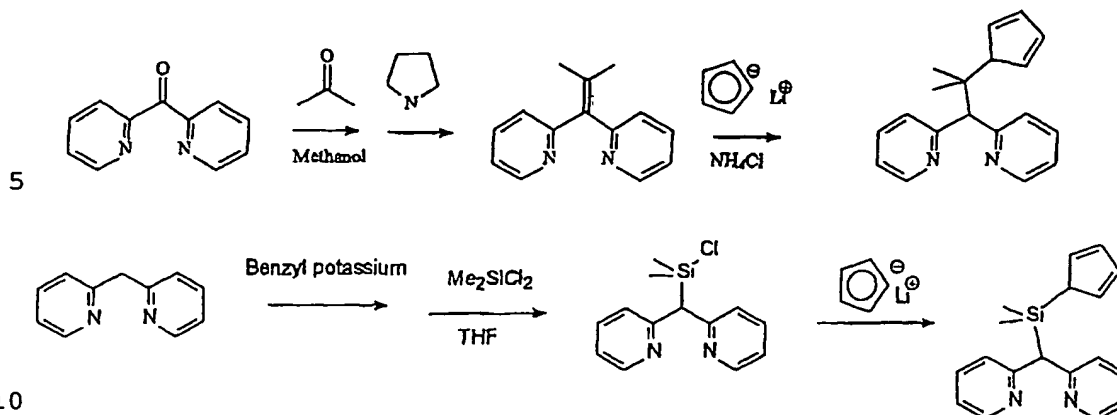
5 to 7 ring membered heterocyclyl (eg pyrrolyl, furanyl and pyrrolidinyl).

The open  $\eta^5$ -ligands used according to the invention may be prepared from readily available starting materials such as di(2-pyridyl) ketone. An  $\eta^5$ -ligand such as dipyridin-2-ylmethane may then be readily prepared by reduction of the ketone functionality using hydrated hydrazine in base or by using a zinc amalgam in acid. If the 3 position of the  $\eta^5$ -ligand chain is to carry a substituent R" then this substituent may conveniently be introduced prior to complete reduction. For example, where a cyclopentadienyl  $\eta$ -ligand group is to be introduced at the 3 position of the  $\eta^5$ -ligand chain, the di(2-pyridyl) ketone may be conveniently be reduced to an alcohol and converted into an excellent leaving group by reaction with tosylate. A cyclopentadienyl group may then be introduced by for example forming a Grignard reagent from chloromethylcyclopentadienyl and reacting this with the dipyridyl tosylate derivative.

Another way to prepare ligands with substituents in the 3 position of the  $\eta^5$ -ligand chain is via the dimethylfulvalene derivative of di(2-pyridylmethane). The dimethylfulvalene derivative may be prepared via reaction of di(2-pyridylketone) with acetone in methanol catalysed by pyrrolidine. Reacting the dimethylfulvalenedipyridyl derivative so obtained with an alkali metal salt of for example, cyclopentadiene or triisopropylsiloxy cyclopentadiene, gives the  $\text{Me}_2\text{C}$  bridged derivatives mentioned. By using an excess of  $\text{Me}_2\text{SiCl}_2$  with the alkali metal salt of the di(2-pyridyl-methanediyl) cation and subsequently reacting with a cyclopentadienyl cation the corresponding  $\text{Me}_2\text{Si}$  bridged derivatives may be obtained.

These reactions are illustrated in schemes below.

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The ligand can be metallated conventionally, eg by reaction with a halide of the metal M, preferably in an organic solvent, eg a hydrocarbon or a hydrocarbon/ether mixture. Bridged ligands may be constructed by reacting an open  $\eta^5$ -ligand with a labile hydrogen at the 3-atom of the  $\eta^5$  chain with a bridging agent (eg  $\text{Si}(\text{CH}_3)_2\text{Cl}_2$ ) or  $\text{Br}(\text{CH}_2)_2\text{Br}$  or with a bridging agent and a further  $\eta$ -ligand (eg a different cyclopentadienyl ligand or with an indenyl, fluorenyl, etc ligand).

$\sigma$ -ligands other than chlorine may be introduced by displacement of chlorine from an  $\eta^5$ -ligand metal chloride by reaction with appropriate nucleophilic reagent (e.g. methyl lithium or methylmagnesium chloride) or using, instead of a metal halide, a reagent such as tetrakisdimethylamidotitanium or metal compounds with mixed chloro and dimethylamido ligands.

As mentioned above, the olefin polymerisation catalyst system of the invention comprises (i) an open  $\eta^5$ -liganded metallocene and normally (ii) an aluminium alkyl compound, or the reaction product thereof.

However, when the metal in the procatalyst is a group 3 transition metal, i.e. Sc, Y, La or Ac, no co-activator is required since such procatalyst species are already in an active form, e.g.  $\text{Cp}_2\text{ScH}$ .

While the aluminium alkyl compound may be an aluminium trialkyl (eg triethylaluminium (TEA)) or an

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aluminium dialkyl halide (eg diethyl aluminium chloride (DEAC)), it is preferably an alumoxane, particularly an alumoxane other than MAO, most preferably an isobutylalumoxane, eg TIBAO (tetraisobutylalumoxane) or  
5 HIBAO (hexaisobutylalumoxane). Alternatively however the alkylated (eg methylated) metallocene procatalysts of the invention (e.g. compounds of formula V wherein Z is alkyl) may be used with other cocatalysts, eg boron compounds such as  $B(C_6F_5)_3$ ,  $C_6H_5N(CH_3)_2H:B(C_6F_5)_4$ ,  
10  $(C_6H_5)_3C:B(C_6F_5)_4$  or  $Ni(CN)_4[B(C_6F_5)_3]_4^{2-}$ .

The metallocene procatalyst and cocatalyst may be introduced into the polymerization reactor separately or together or, more preferably they are pre-reacted and their reaction product is introduced into the  
15 polymerization reactor.

If desired the procatalyst, procatalyst/cocatalyst mixture or a procatalyst/cocatalyst reaction product may be used in unsupported form, i.e. metallocene and MAO can be precipitated without an actual carrier material  
20 and used as such. However the metallocene procatalyst or its reaction product with the cocatalyst is preferably introduced into the polymerization reactor in supported form, eg impregnated into a porous particulate support.

25 The particulate support material used is preferably an organic or inorganic material, e.g. a polymer (such as for example polyethylene, polypropylene, an ethylene-propylene copolymer, another polyolefin or polystyrene or a combination thereof). Such polymeric supports may  
30 be formed by precipitating a polymer or by a prepolymerization, eg of monomers used in the polymerization for which the catalyst is intended. However, the support is especially preferably a metal or pseudo metal oxide such as silica, alumina or zirconia  
35 or a mixed oxide such as silica-alumina, in particular silica, alumina or silica-alumina. Particularly preferably, the support material is acidic, e.g. having

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an acidity greater than or equal to silica, more preferably greater than or equal to silica-alumina and even more preferably greater than or equal to alumina. The acidity of the support material can be studied and compared using the TPD (temperature programmed desorption of gas) method. Generally the gas used will be ammonia. The more acidic the support, the higher will be its capacity to adsorb ammonia gas. After being saturated with ammonia, the sample of support material is heated in a controlled fashion and the quantity of ammonia desorbed is measured as a function of temperature.

Especially preferably the support is a porous material so that the metallocene may be loaded into the pores of the support, e.g. using a process analogous to those described in WO94/14856 (Mobil), WO95/12622 (Borealis) and WO96/00243 (Exxon). The particle size is not critical but is preferably in the range 5 to 200  $\mu\text{m}$ , more preferably 20 to 80  $\mu\text{m}$ .

Before loading, the particulate support material is preferably calcined, ie heat treated, preferably under a non-reactive gas such as nitrogen. This treatment is preferably at a temperature in excess of 100°C, more preferably 200°C or higher, e.g. 200-800°C, particularly about 300°C. The calcination treatment is preferably effected for several hours, e.g. 2 to 30 hours, more preferably about 10 hours.

The support may be treated with an alkylating agent before being loaded with the metallocene. Treatment with the alkylating agent may be effected using an alkylating agent in a gas or liquid phase, e.g. in an organic solvent for the alkylating agent. The alkylating agent may be any agent capable of introducing alkyl groups, preferably  $\text{C}_{1-6}$  alkyl groups and most especially preferably methyl groups. Such agents are well known in the field of synthetic organic chemistry. Preferably the alkylating agent is an organometallic

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compound, especially an organoaluminium compound (such as trimethylaluminium (TMA), dimethyl aluminium chloride, triethylaluminium) or a compound such as methyl lithium, dimethyl magnesium, triethylboron, etc.

5       The quantity of alkylating agent used will depend upon the number of active sites on the surface of the carrier. Thus for example, for a silica support, surface hydroxyls are capable of reacting with the alkylating agent. In general, an excess of alkylating  
10       agent is preferably used with any unreacted alkylating agent subsequently being washed away.

Where an organoaluminium alkylating agent is used, this is preferably used in a quantity sufficient to provide a loading of at least 0.1 mmol Al/g carrier, especially at least 0.5 mmol Al/g, more especially at  
15       least 0.7 mmol Al/g, more preferably at least 1.4 mmol Al/g carrier, and still more preferably 2 to 3 mmol Al/g carrier. Where the surface area of the carrier is particularly high, lower aluminium loadings may be used.  
20       Thus for example particularly preferred aluminium loadings with a surface area of 300-400 m<sup>2</sup>/g carrier may range from 0.5 to 3 mmol Al/g carrier while at surface areas of 700-800 m<sup>2</sup>/g carrier the particularly preferred range will be lower.

25       Following treatment of the support material with the alkylating agent, the support is preferably removed from the treatment fluid and any excess treatment fluid is allowed to drain off.

The optionally alkylated support material is loaded  
30       with the procatalyst, preferably using a solution of the procatalyst in an organic solvent therefor, e.g. as described in the patent publications referred to above. Preferably, the volume of procatalyst solution used is from 50 to 500% of the pore volume of the carrier, more  
35       especially preferably 80 to 120%. The concentration of procatalyst compound in the solution used can vary from dilute to saturated depending on the amount of

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metallocene active sites that it is desired be loaded into the carrier pores.

The active metal (ie. the metal of the procatalyst) is preferably loaded onto the support material at from  
5 0.1 to 4%, preferably 0.5 to 3.0%, especially 1.0 to 2.0%, by weight metal relative to the dry weight of the support material.

After loading of the procatalyst onto the support material, the loaded support may be recovered for use in  
10 olefin polymerization, e.g. by separation of any excess procatalyst solution and if desired drying of the loaded support, optionally at elevated temperatures, e.g. 25 to 80°C.

Alternatively, a cocatalyst, e.g. an alumoxane or  
15 an ionic catalyst activator (such as a boron or aluminium compound, especially a fluoroborate) may also be mixed with or loaded onto the catalyst support material. This may be done subsequently or more preferably simultaneously to loading of the procatalyst,  
20 for example by including the cocatalyst in the solution of the procatalyst, by contacting the procatalyst loaded support material with a solution of the cocatalyst or catalyst activator, e.g. a solution in an organic solvent, or by first impregnating the cocatalyst with a  
25 support and then contacting the cocatalyst impregnated support with a solution of the procatalyst or neat procatalyst (e.g. as described in WO96/32423).

Alternatively however any such further material may be added to the procatalyst loaded support material in the  
30 polymerization reactor or shortly before dosing of the catalyst material into the reactor.

In this regard, as an alternative to an alumoxane it may be preferred to use a fluoroborate catalyst activator for the alkylated procatalysts, especially a  
35  $B(C_6F_5)_3$  or more especially a  $^aB(C_6F_5)_4$  compound, such as  $C_6H_5N(CH_3)_2H:B(C_6F_5)_4$  or  $(C_6H_5)_3C:B(C_6F_5)_4$ . Other borates of general formula (cation)<sub>a</sub> (borate)<sub>b</sub> where a and b are



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positive numbers, may also be used.

Where such a cocatalyst or catalyst activator is used, it is preferably used in a mole ratio to the metallocene of from 0.1:1 to 10000:1, especially 1:1 to 50:1, particularly 1:2 to 30:1. More particularly, where an alumoxane cocatalyst is used, then for an unsupported catalyst the aluminium:metallocene metal (M) molar ratio is conveniently 2:1 to 10000:1, preferably 50:1 to 1000:1. Where the catalyst is supported the Al:M molar ratio is conveniently 2:1 to 10000:1 preferably 50:1 to 400:1. Where a borane cocatalyst (catalyst activator) is used, the B:M molar ratio is conveniently 2:1 to 1:2, preferably 9:10 to 10:9, especially 1:1. When a neutral triarylboron type cocatalyst is used the B:M molar ratio is typically 1:2 to 500:1, however some aluminium alkyl would normally also be used. When using ionic tetraaryl borate compounds, it is preferred to use carbonium rather than ammonium counterions or to use B:M molar ratio 1:1.

Where the further material is loaded onto the procatalyst loaded support material, the support may be recovered and if desired dried before use in olefin polymerization.

The olefin polymerized in the method of the invention is preferably ethylene or an alpha-olefin or a mixture of ethylene and an  $\alpha$ -olefin or a mixture of alpha olefins, for example  $C_{2-20}$  olefins, e.g. ethylene, propene, n-but-1-ene, n-hex-1-ene, 4-methyl-pent-1-ene, n-oct-1-ene- etc. The olefins polymerized in the method of the invention may include any compound which includes unsaturated polymerizable groups. Thus for example unsaturated compounds, such as  $C_{6-20}$  olefins (including cyclic and polycyclic olefins (e.g. norbornene)), and polyenes, especially  $C_{6-20}$  dienes, may be included in a comonomer mixture with lower olefins, e.g.  $C_{2-5}$   $\alpha$ -olefins. Diolefins (ie. dienes) are suitably used for introducing long chain branching into the resultant

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polymer. Examples of such dienes include  $\alpha,\omega$  linear dienes such as 1,5-hexadiene, 1,6-heptadiene, 1,8-nonadiene, 1,9-decadiene, etc.

5 In general, where the polymer being produced is a homopolymer it will preferably be polyethylene or polypropylene. Where the polymer being produced is a copolymer it will likewise preferably be an ethylene or propylene copolymer with ethylene or propylene making up the major proportion (by number and more preferably by  
10 weight) of the monomer residues. Comonomers, such as  $C_{4-6}$  alkenes, will generally be incorporated to contribute to the mechanical strength of the polymer product.

Usually metallocene catalysts yield relatively  
15 narrow molecular weight distribution polymers; however, if desired, the nature of the monomer/monomer mixture and the polymerization conditions may be changed during the polymerization process so as to produce a broad bimodal or multimodal molecular weight distribution  
20 (MWD) in the final polymer product. In such a broad MWD product, the higher molecular weight component contributes to the strength of the end product while the lower molecular weight component contributes to the processability of the product, e.g. enabling the product  
25 to be used in extrusion and blow moulding processes, for example for the preparation of tubes, pipes, containers, etc.

A multimodal MWD can be produced using a catalyst material with two or more different types of active  
30 polymerization sites, e.g. with one such site provided by the metallocene on the support and further sites being provided by further catalysts, e.g. Ziegler catalysts, other metallocenes, etc. included in the catalyst material.

35 Polymerization in the method of the invention may be effected in one or more, e.g. 1, 2 or 3, polymerization reactors, using conventional

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polymerization techniques, e.g. gas phase, solution phase, slurry or bulk polymerization.

In general, a combination of slurry (or bulk) and at least one gas phase reactor is often preferred, particularly with the reactor order being slurry (or bulk) then one or more gas phase.

For slurry reactors, the reaction temperature will generally be in the range 60 to 110°C (e.g. 85-110°C), the reactor pressure will generally be in the range 5 to 80 bar (e.g. 50-65 bar), and the residence time will generally be in the range 0.3 to 5 hours (e.g. 0.5 to 2 hours). The diluent used will generally be an aliphatic hydrocarbon having a boiling point in the range -70 to +100°C. In such reactors, polymerization may if desired be effected under supercritical conditions.

For gas phase reactors, the reaction temperature used will generally be in the range 60 to 115°C (e.g. 70 to 110°C), the reactor pressure will generally be in the range 10 to 25 bar, and the residence time will generally be 1 to 8 hours. The gas used will commonly be a non-reactive gas such as nitrogen together with monomer (e.g. ethylene).

For solution phase reactors, the reaction temperature used will generally be in the range 130 to 270°C, the reactor pressure will generally be in the range 20 to 400 bar and the residence time will generally be in the range 0.005 to 1 hour. The solvent used will commonly be a hydrocarbon with a boiling point in the range 80-200°C.

Generally the quantity of catalyst used will depend upon the nature of the catalyst, the reactor types and conditions and the properties desired for the polymer product. Conventional catalyst quantities, such as described in the publications referred to herein, may be used.

All publications referred to herein are hereby incorporated by reference.

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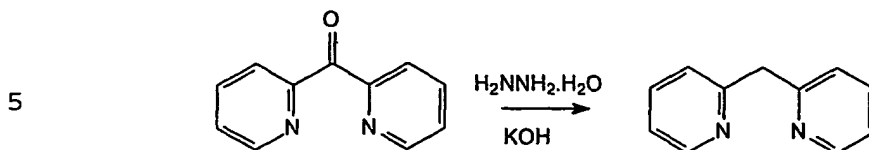
The invention will now be illustrated further by reference to the following non-limiting Examples.

## 5      **General Considerations**

All operations were carried out in argon or nitrogen atmosphere using standard Schlenk, vacuum and dry box techniques. Solvents were dried with potassium  
10      benzophenone ketyl and distilled under argon prior to use. 1.5.7-triaza[4.4.0]bicyclo-dec-5-ene (Fluka),  
(nBuCp)<sub>2</sub>ZrCl<sub>2</sub> (Witco) and ZrCl<sub>4</sub> (Aldrich) were used without further purification. Benzyl potassium was prepared according to literature. The NMR spectra were  
15      recorded using JEOL JNM-EX 270 MHz FT NMR spectrometer with tetramethylsilane (TMS) as an internal reference. The mass spectra were recorded at Fortum Oil and Gas Oy, Analytical Research. The direct inlet spectra were produced by VG TRIO 2 quadrupole mass spectrometer in  
20      electron impact ionisation mode (70eV). The GC-MS analyses were performed using HewLett Packard 6890/5973 Mass Selective Detector in electron impact ionisation mode (70eV) and equipped with a silica capillary column (30m x 0.25mm id.). The polymerisation tests were  
25      carried out using MAO, 30% solution in toluene purchased from Albermarle. Test polymerisations were carried out in pentane at 80°C with no hydrogen present using an Al/Zr ratio of 1000 unless otherwise stated. A Buchi 2L stirred reactor with mantle heating was used for the  
30      polymerisation tests.

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## Example 1

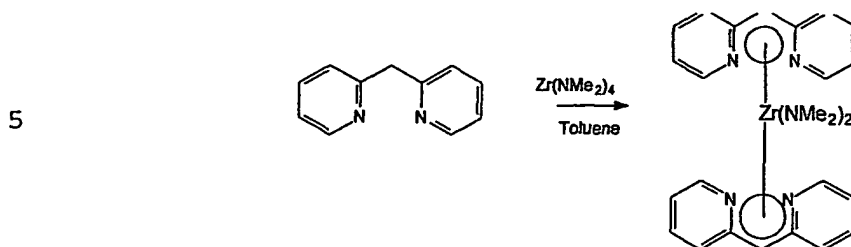


## DPM-H Synthesis of dipyridin-2-ylmethane

10 Solid KOH (9.4 g, 167.7 mmol) was dissolved in 15 ml of distilled water and poured into an autoclave reactor (Parr pressure reactor) under nitrogen atmosphere. Di(2-pyridyl) ketone (15.0 g, 81.4 mmol) was weighed and introduced into the reactor. Hydrazine monohydrate (6.1  
15 ml, 185.7 mmol) was poured into the reaction mixture and the reactor closed. The reactor was mounted on a Parr heater unit and the reaction mixture stirred for 18h at 150°C at 28 bar. After 1 hour the temperature was 150°C and the pressure 5 bar. After 18h heating and stirring  
20 the temperature was 151°C and the pressure inside the reactor 28 bar. After the reaction was complete, the cooled reactor was opened at air atmosphere and the yellowish liquid obtained neutralized with 1 M HCl (aq.) and extracted with 3x50 ml chloroform. Organic phase was  
25 washed with 3x30 ml of brine and dried over MgSO<sub>4</sub>. Solvents were removed in a vacuum and the crude product distilled in a vacuum to obtain a yellow liquid with b.p. 80-85°C/0.06 mbar. Yield: 9.8 g (72%). <sup>1</sup>H-NMR in CDCl<sub>3</sub>; δ: 8.48 (m, 2H); 7.51 (m, 2H); 7.19 (t, 2H); 7.04  
30 (m, 2H); 4.29 (s, 2H). EIMS analysis showed parent ion of the title compound C<sub>11</sub>H<sub>10</sub>N<sub>2</sub> corresponding to molecular weight M<sup>+</sup>=170.21 g mol<sup>-1</sup>.

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## Example 2



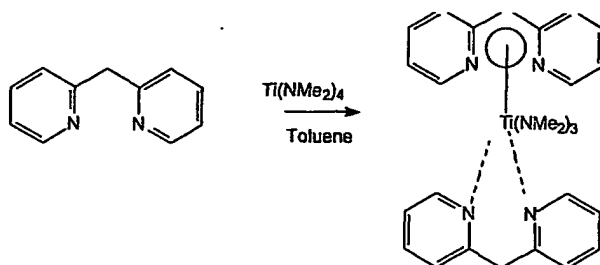
10 (DPM)<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub> Synthesis of bis(dipyridin-2-ylmethanyl)  
dimethylamido zirconium

Dipyridin-2-ylmethane (1.94 g, 11.36 mmol) dissolved in  
50 ml of dry toluene was added inertly into a solution  
15 of tetrakis dimethylamido zirconium [Zr(NMe<sub>2</sub>)<sub>4</sub>] (1.52g,  
5.68 mmol) in 50 ml of dry toluene at room temperature  
over five minutes to obtain a bright red coloured  
slurry. The slurry was then refluxed for 16h to obtain a  
bright red solution. From the cooled reaction vessel all  
20 solvents were removed in a vacuum and the product washed  
with 3 x 20 ml of dry pentane. Finally all solvents were  
removed in a vacuum to give a red solid product. Yield  
2.04 g (69.4%). The product shows fluxional behaviour  
and coalescence in the NMR time scale. NMR spectra were  
25 recorded at +25°C and at +70°C. <sup>1</sup>H-NMR in C<sub>6</sub>D<sub>6</sub> at 70°C δ:  
7.52 (broad, 4H), 6.75 (t, 4H), 6.50 (d, 4H), 5.97 (t,  
4H), 5.02 (s, 2H), 3.2 (s, 12H). <sup>13</sup>C-NMR in C<sub>6</sub>D<sub>6</sub> at +70°C  
δ: 154.2, 143.0, 131.8, 123.1, 108.5, 94.9, 45.2. EIMS  
analysis of the title compound C<sub>26</sub>H<sub>30</sub>N<sub>6</sub>Zr showed parent  
30 ion peak at M<sup>+</sup>=517.78 g mol<sup>-1</sup>. Elemental analysis  
calculated: C 60.31%, N 16.23% H 5.84%. Elemental  
analysis found: C 59.4%, N 15.9% H 5.6%.

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## Example 3

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10 (DPM) (DPM-H)Ti(NMe<sub>2</sub>)<sub>3</sub> - Synthesis of (dipyridin-2-ylmethanyl) (dipyridin-2-ylmethylene) trismethylamido titanium

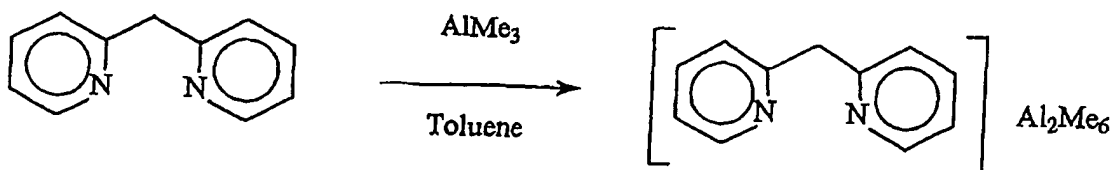
15 Dipyridin-2-ylmethane (1.94 g, 11.36 mmol) dissolved in 30 ml of dry toluene was added inertly into a solution of tetrakis dimethylamido titanium [Ti(NMe<sub>2</sub>)<sub>4</sub>] (1.27g, 5.68 mmol) in 50 ml dry toluene at -30°C over 20 minutes to obtain a black red solution. The solution was refluxed for 4 h and all solvents removed in a vacuum to

20 give a dark brown oil. Yield 2.9 g (99%). <sup>1</sup>H-NMR in C<sub>6</sub>D<sub>6</sub> δ: 8.59 (d, 2H), 7.72 (d, 2H), 7.24 (dd, 2H), 7.13 (dd, 2H), 6.89 (d, 2H), 6.87 (d, 2H), 6.69 (dd, 2H), 6.08 (dd, 2H), 5.61 (s, 1H), 4.55 (s, 2H) <sup>13</sup>C-NMR in C<sub>6</sub>D<sub>6</sub> δ: 160.3, 154.9, 149.6, 147.5, 135.9, 133.1, 123.7, 123.6,

25 121.2, 109.0, 93.2, 47.9, 46.4. EIMS analysis of the title compound C<sub>28</sub>H<sub>37</sub>N<sub>7</sub>Ti showed a parent ion peak at M=519.53 g mol<sup>-1</sup>.

## Example 4

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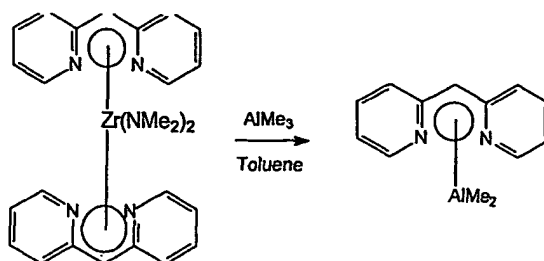
(DPM)Al<sub>2</sub>Me<sub>3</sub> Synthesis of (dipyridin-2-ylmethane)  
dimethylaluminum

Into a solution of di(pyridin-2-ylmethane) (1.0g, 5.9 mmol) in 50 ml of toluene was added trimethylaluminium (4.5g, 6.2 mmol, 10% w solution heptane) at -30°C over 10 minutes. The resulting solution was stirred at ambient temperature for 16 hours. Solvents were removed under vacuum and the yellow solid raw product washed with pentane and then with hot (+60°C) heptane and finally dried under vacuum yielding a light yellow solid. Yield 1.5g (80.9%). The product decomposed during the EIMS analysis. The spectrum however, showed the decomposition pattern of the parent ion of the title compound C<sub>17</sub>H<sub>28</sub>Al<sub>2</sub>N<sub>2</sub> with peaks at M=(314.39), 283.0, 226.3, 211.0 and 169.2 g mol<sup>-1</sup>. <sup>1</sup>H-NMR in C<sub>6</sub>D<sub>6</sub> δ: 8.68 (d, 2H), 6.75 (dd, 2H), 6.49 (d, 2H), 5.95 (dd, 2H), 5.05 (s, 2H), -0.01 (s, 18H). <sup>13</sup>C-NMR in C<sub>6</sub>D<sub>6</sub> δ: 158.7, 148.5, 140.6, 126.9, 123.6, 42.3, -5.6.



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## Example 5



(DPM)AlMe<sub>3</sub> Synthesis of dipyridin-2-ylmethanyl)  
dimethylaluminum

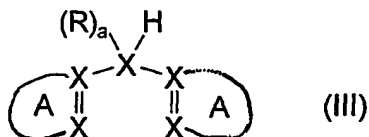
Into a solution of *bis*(dipyridin-2-ylmethanyl)dimethylamido zirconium (0.9g, 1.7 mmol) dissolved in 50 ml of toluene was added trimethylaluminum (3.5g, 89.6 mmol, 20%w solution in pentane) at -30°C and stirred for 3 hours at ambient temperature and then refluxed for 1 hour. The cooled reaction mixture was evaporated dry and the resulting new product extracted with pentane. The pentane was removed under vacuum yielding a red-brown solid product. Yield 0.12g (31.2%). <sup>1</sup>H-NMR in C<sub>6</sub>D<sub>6</sub> δ: 7.37 (d, 2H), 6.66 (dd, 2H), 6.43 (d, 2H), 5.90 (dd, 2H), 5.02 (s, 1H), -0.21 (s, 6H). <sup>13</sup>C-NMR in C<sub>6</sub>D<sub>6</sub> δ: 155.1, 141.1, 139.2, 122.6, 110.6, 88.4, 41.5. EIMS analysis of the title compound C<sub>13</sub>H<sub>15</sub>AlN<sub>2</sub> showed a parent ion peak at M=226.26g mol<sup>-1</sup>. Elemental analysis of aluminium revealed the presence of 12.7%w Al in the product. Amount of Al calculated is 11.93%wt.

Polymerisation Results  
HDPE Polymerisations

Polym type	Complex Ex	cat/umo 1	cocat	polym/g	Activity	Mw/(g/mol) (GPC)	Mw/Mn (GPC)
COPO	2	10	MAO	2	4	586000	96.9
HOPO	2	10	MAO	2	4	842000	84.4
HOPO	3	10	MAO	10	42	-	-
HOPO	4	10	MAO	0	-	-	-
HOPO	5	10	MAO	0	-	-	-

Claims

1. A metallocene procatalyst compound comprising a group III element or a group 3 to 8 transition metal  $\eta$ -bonded by an open  $\eta^5$ -ligand having at least two heteroatoms in the five atom  $\eta^5$  chain and having an unsaturated ring fused to the first and second atoms of the  $\eta^5$  chain and a further unsaturated ring fused to the fourth and fifth atoms of the  $\eta^5$  chain.
2. A metallocene procatalyst compound as claimed in claim 1 wherein the  $\eta^5$ -ligand with which the group III element or a group 3 to 8 metal is complexed is a compound of formula III



where  $\begin{array}{c} \text{X} \\ \text{A} \\ \text{X} \end{array}$  is an optionally substituted 5 to 12 membered ring;

each X independently is C, N, P, B or Si, at least two X's being heteroatoms;

a is 0 or 1;

R is a  $C_{1-16}$  hydrocarbyl, a tri  $C_{1-8}$  hydrocarbylsilyl or a tri  $C_{1-8}$  hydrocarbylsiloxy group or a group  $R^a R^b$  where  $R^a$  is a 1 to 4 atom bridge and  $R^b$  is a group capable of  $\sigma$ -bonding or  $\eta$ -bonding a transition metal.

3. A metallocene procatalyst as claimed in claim 2 wherein  $R^b$  is an  $\eta$ -bonding ligand selected from a homo or heterocyclic cyclopentadienyl, indenyl, fluorenyl, octahydrofluorenyl, methylcyclopentadienyl, 1,2-dimethylcyclopentadienyl, pentamethylcyclopentadienyl, pentyl-cyclopentadienyl, 2-dimethyl-tertbutylsiloxy-inden-1-yl,

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n-butylcyclopentadienyl, 1,3-dimethylcyclopentadienyl, 4,7-dimethylindenyl, 1-ethyl-2-methylcyclopentadienyl, tetrahydroindenyl, and methoxycyclopentadienyl or a  $\sigma$ -ligand selected from halogenides, hydrogen, tri- $C_{1-12}$  hydrocarbyl-silyl or -siloxy, tri- $C_{1-6}$  hydrocarbylphosphimido,  $C_{1-12}$  hydrocarbyl or hydrocarbyloxy, di- $C_{1-6}$  hydrocarbylamido, and 5 to 7 ring membered heterocyclyl, or an amido group).

4. A metallocene procatalyst compound as claimed in claim 2 or 3 wherein the ring  $\begin{array}{c} \text{X} \\ \text{A} | \\ \text{X} \end{array}$  is 6 or 10 membered.

5. A metallocene procatalyst compound as claimed in any one of claims 2 to 4 wherein the ring  $\begin{array}{c} \text{X} \\ \text{A} | \\ \text{X} \end{array}$

is optionally substituted by at least group one  $R'$  where each  $R'$  which may be the same or different is a  $R^+$ ,  $OR^+$ ,  $SR^+$ ,  $NR_2^+$  or  $PR_2^+$  group where each  $R^+$  is a  $C_{1-16}$  hydrocarbyl group, a tri- $C_{1-8}$  hydro-carbylsilyl group or a tri- $C_{1-8}$  hydrocarbylsiloxy group.

6. A metallocene procatalyst compound as claimed in any one of claims 2 to 5 wherein the terminal X atoms are N and the other X atoms are C.

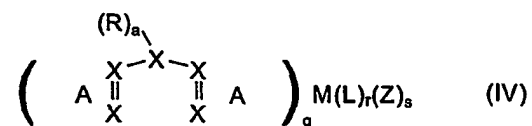
7. A metallocene procatalyst compound as claimed in any one of claims 2 to 6 wherein  $\begin{array}{c} \text{X} \\ \text{A} | \\ \text{X} \end{array}$  is pyridyl.

8. A metallocene procatalyst compound as claimed in any one of claims 2 to 7 wherein R is a group  $R^a R^b$  in which  $R^a$  is a 1 to 4 atom bridge and  $R^b$  is a cyclopentadienyl, indenyl, fluorenyl, octahydrofluorenyl, methylcyclopentadienyl, 1,2-dimethylcyclopentadienyl,

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pentamethylcyclopentadienyl, pentyl-cyclopentadienyl, 2-dimethyl-tertbutylsiloxy-inden-1-yl, n-butylcyclopentadienyl, 1,3-dimethylcyclopentadienyl, 4,7-dimethylindenyl, 1-ethyl-2-methylcyclopentadienyl, tetrahydroindenyl, and methoxycyclopentadienyl, optionally substituted by a group R' where each R' which may be the same or different is a R<sup>+</sup>, OR<sup>+</sup>, SR<sup>+</sup>, NR<sub>2</sub><sup>+</sup> or PR<sub>2</sub><sup>+</sup> group where each R<sup>+</sup> is a C<sub>1-16</sub> hydrocarbyl group, a tri-C<sub>1-8</sub>hydro-carbylsilyl group or a tri-C<sub>1-8</sub>-hydrocarbylsiloxy group.

9. A metallocene procatalyst compound as claimed in any one of claims 2 to 8 of formula (IV)



where  $\begin{array}{c} \text{X} \\ | \\ \text{A} \end{array}$  X, (R)<sub>a</sub>, and X are as hereinbefore defined;  
q is 1, 2 or 3;

M is a group III element or a group 3 to 8 transition metal

L is a η-ligand;

r is zero, 1 or 2;

Z is a σ-ligand; and

s is zero or a positive integer having a value of up to 3.

10. A metallocene procatalyst as claimed in claim 9 wherein M is Ti, Zr, Hf or Al.

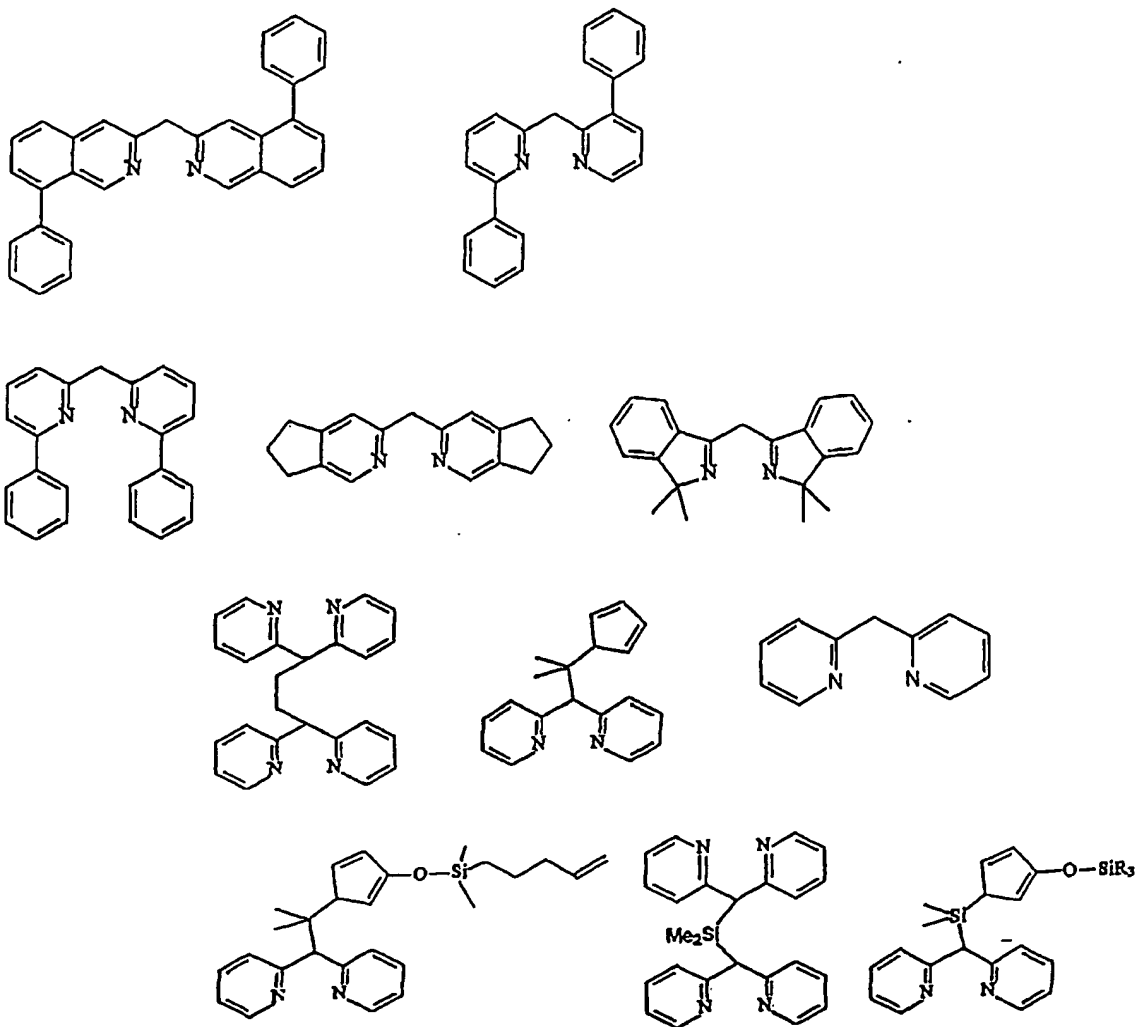
11. A metallocene procatalyst as claimed in claim 9 or 10 wherein Z is a halogenide, C<sub>1-12</sub>-hydrocarbyl or di-C<sub>1-6</sub>-hydrocarbyl amido.

12. A metallocene procatalyst as claimed in any one of

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claims 9 to 11 wherein L is cyclopentadienyl, indenyl, fluorenyl, octahydrofluorenyl, methylcyclopentadienyl, 1,2-dimethylcyclopentadienyl, pentamethylcyclopentadienyl, pentyl-cyclopentadienyl, 2-dimethyl,tertbutylsiloxy-inden-1-yl, n-butylcyclopentadienyl, 1,3-dimethylcyclopentadienyl, 4,7-dimethylindenyl, 1,-ethyl-2-methylcyclopentadienyl, tetrahydroindenyl, and methoxycyclopentadienyl.

13. A metallocene procatalyst as claimed in any one of claims 1 to 12 wherein said open  $\eta^5$ -ligand is



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14. An olefin polymerisation catalyst system comprising or produced by reaction of (i) a metallocene procatalyst compound as claimed in any one of claims 1 to 13 and (ii) a co-catalyst.

15. A process for olefin polymerisation comprising polymerising an olefin in the presence of a metallocene procatalyst as claimed in any one of claims 1 to 13.

16. The use of a metallocene compound as claimed in any one of claims 1 to 13 in olefin polymerization, especially ethylene or propylene, more especially ethylene, polymerisation or copolymerisation.

17. An olefin polymer produced by a polymerisation catalysed by a metallocene compound as claimed in any one of claims 1 to 13.